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PROCEDURE FOR DECONVOLUTION OF THE SECOND PEAK FOR ORGANIC SULPHUR 2 (S_{o2}) AND PYRITIC SULPHUR (S_{p2}) IN INFRARED SO_x SPECTROCHRONOGRAM OF COALS

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MICROMEDIA

PROCEDURE FOR DECONVOLUTION OF THE SECOND PEAK FOR ORGANIC SULPHUR 2 (S_{o2}) AND PYRITIC SULPHUR (S_{p2}) IN INFRARED SO_x SPECTROCHRONOGRAM OF COALS

by

K.S. Moon*

SUMMARY

A patent-pending procedure was developed in CANMET for the quantitative determination of differenc sulphur forms in coals. A prototype instrument is being developed by Barringer Research Laboratory Ltd. under a contract agreement. At the present time, procedures that give good reprductibility of IR spectrochronograms for SO_x compounds are in place. Software for a deconvolution of the multi-peak spectrochronogram is being tested. It was found, however, that a deconvolution of the second peak for organic sulphur 2 (S_{o2}) and pyritic sulphur (S_{p2}) might not be practical due to the overlap of the two peaks. Some possible alternate procedures are developed in the present discussion. The procedure requires advanced knowledge of the constant ratio, k, of S_{o1} to S_{p2} for the coal sample. There is an indication that the organic sulphur content in different coals consists of organic sulphur 1 which is constant and organic sulphur 2 which is proportional to pyritic sulphur. This procedure is limited by its requirement of the prior knowledge of the constant ratio, k. When the mathematical deconvolution technique under development is perfected, however, the present procedure will lose its usefulness.

Keywords: Coal Analysis, Sulphur forms, Organic Sulphur, Pyritic Sulphur.

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DÉROULEMENT DE LA DÉCONVOLUTION DU DEUXIÈME PIC DU SOUFRE D'ORIGINE ORGANIQUE 2 (S_{o2}) ET DU SOUFRE PYRITEUX (S_{p2}) DANS LES SPECTROCHRONOGRAMMES INFRAGOUGES DE L'ANHYDRIDE SULFUREUX (SO_x), PRÉSENT DANS LES CHARBONS

par

K.S. Moon*

RÉSUMÉ

Un mode opératoire devant être breveté sous peu a été développé à CANMET en vue de déterminer quantitativement les différentes formes du soufre présent dans les charbons. En vertu d'une entente, Barringer Research Laboratory Ltd. réalise en sous-traitance, le dévloppement du prototype de l'appareil. À l'heure actuelle, le mode opératoire qui permet une bonne reproductibilité des spectrochronogrammes infrarouges des composés de l'anhydride sulfureux (SO_x) est établi. Un logiciel relatif au déroulement de la déconvolution du spectrochronogramme à pics multiples est à l'essai. Cependant, on a découvert que la déconvolution du deuxième pic du soufre d'origine organique (S_{o2}) et du soufre pyriteux (S_{p2}) peut ne pas s'avérer pratique en raison du chevauchement des deux pics. Quelques modes opératoires de rechange sont décrits dans cette étude. Le mode opératoire exige une connaissance préalable du rapport constant k, de S_{o1} et de S_{p2} présents dans l'échantillon de charbon. Selon toute apparence, la teneur en soufre d'origine organique de différents charbons consiste de soufre d'origine organique 1, qui est constant, et de soufre d'origine organique 2, qui est en proportion avec le soufre pyriteux. Ce mode opératoire est limité car il exige une connaissance préalable du rapport constant, k. Quand la technique de déconvolution mathématique qui est en développement à l'heure actuelle aura été perfectionnée, le mode opératoire susmentionné ne sera plus utile.

Mots-clé : Analyse du charbon, formes du soufre, soufre d'origine organique, soufre pyriteux.

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DEFINITION OF SYMBOLS

M_i : Sample Weight for ith component

W_i : Sulphur Weight for ith component

A_i : Peak Area for ith component in arbitrary unit per mg of coal sample

S_i : Fractional Content of ith sulphur component in coal sample

* : Extra sample added to the coal sample

i = 1 : Peak 1 Organic Sulphur

2 : Peak 2 Sulphur

T : Total Sulphur

σ1 : Peak 1 Organic Sulphur

σ2 : Peak 2 Organic Sulphur

σT : Total Organic Sulphur

p1 : Peak 1 Pyritic Sulphur

p2 : Peak 2 Pyritic Sulphur

pT : Total Pyritic Sulphur

SO_4 : Sulphatic Sulphur

INTRODUCTION

In developing a prototype CANMET SULPHUR FORM ANALYSER, the procedures that result in good reproductibility of IR spectrochronograms for SO_x compounds are in place. Software for a deconvolution of the multi-peak spectrochronogram is being tested. The following is a brief list of what remains to be done for the completion of the project:

1. Test of deconvolution algorithm for synthetic curves; perturbation of variables, asymmetric Laurentian Distribution, baseline with slope
2. Improvement of spectrochronogram reproducibility
3. Duplicate sulphur form analyses for standard coal samples
4. Generation of IR spectrochronogram data bank for various coals that contain differing amounts of different sulphur forms
5. Establishment of the procedure for deconvolution of the second peak for organic sulphur 2 (S_{o2}) and pyritic sulphur (S_{p2})
6. Determination of elemental sulphur (S°) and sulphate sulphur (S_{SO4})
7. Set-up of prototype instrument hardware
8. Establishment of standard analysis procedure
9. Preparation of operating manual
10. Delivery of prototype instrument with operating manual and project report

The progress report by Dancziger, M. (1) of Barringer Research Ltd. (BRL) indicated that part of the organic sulphur appears together with pyritic sulphur at peak positions close by, making deconvolution difficult. In case that deconvolution of the second peak for organic sulphur 2 (S_{o2}) and pyritic sulphur (S_{p2}) is not practical due to the overlap of the two peaks, some possible alternate procedures are discussed in the following section. The procedure requires prior knowledge of the constant ratio, k, of S_{o1} to S_{p2} for the coal sample.

RESULTS AND DISCUSSIONS

In the present study (1), known quantities of a pyrite (M_{p2}^*) sample were added to coal sample to make up a 100 mg total sample weight. The relationship between peak area and sulphur content in the mixed sample is developed in the following CASE I. However, a simpler algorithm may be used to describe the same relationship, as indicated in CASE II, if one uses a constant amount of coal sample with different amount of pyrite to prepare the mixed sample.

CASE I. $W_{o1} + W_{o2} + W_{p2} = (100 - M_{p2}^*)(S_{o1} + S_{o2} + S_{p2})$
(where W_{SO4} is negligible)

$W_T = W_{o1} + W_{o2} + W_{p2} + W_{p2}^*$

$W_{p2} = c \times S_{p2}^* \times M_{p2}^*$

Where c = 0.88 (pyrite purity, but should be 1.000 for pure FeS_2)

$S_{p2}^* = 2 \times 32.06 / (55.8475 + 2 \times 32.06) = 0.53448$

$W_{p2}^* = 0.88 \times 0.53448 \times M_{p2}^*$

$= 0.47034 \times Mp_2^*$

$W_{o1} + W_{o2} + W_{p2} = (100 - M_{p2}^*)(S_{o1} + S_{o2} + S_{p2})$

$W_T = (100 - M_{p2}^*)(S_{o1} + S_{o2} + S_{p2}) + 0.47034 \times M_{p2}^*$

$= 100 \times (S_{o1} + S_{o2} + S_{p2})$

$+ (0.47034 - (S_{o1} + S_{o2} + S_{p2})) \times M_{p2}^*$

$= (100 \times S_{o1} - S_{o1} \times M_{p2}^*)$

$+ (100 \times (S_{o2} + S_{p2}) + (0.47034 - (S_{o2} + S_{p2})) \times M_{p2}^*)$

$= (100 \times S_{o1} - S_{o1} \times W_{p2}^* / 0.47034)$

$+ (100 \times (S_{o2} + S_{p2}) + (0.47034 - (S_{o2} + S_{p2})) \times W_{p2}^* / 0.47034)$

$= W_1 + W_2$

Where $W_1 = 100 \times S_{o1} - S_{o1} \times M_{p2}^*$

$= 100 \times S_{o1} - S_{o1} \times W_{p2}^* / 0.47034$

$= (47.034 + W_{o1} + W_{o2} + W_{p2} - W_T) \times S_{o1} / 0.47034$

$W_2 = 100 \times (S_{o2} + S_{p2}) + (0.47034 - (S_{o2} + S_{p2})) \times W_{p2}^* / 0.47034$

$= -(47.034 + W_{o1} + W_{o2} + W_{p2}) \times S_{o1} / 0.47034 + (1 + S_{o1} / 0.47034) \times W_T$

$= ((47.034 + W_{o1} + Wo_2 + W_{p2}) \times (S_{o1} + S_{p2}) - (W_{o1} + W_{o2} + W_{p2})) / 0.47034 + (1 - (S_{o2} + S_{p2}) / 0.47034) \times W_T$

$W_i = a \times A_i$

CASE II. $W_{o1} + W_{o2} + W_{p2} = 100 \times (S_{o1} + S_{o2} + S_{p2})$: constant for a coal (where S_{SO4} is negligible)

$W_T = W_{o1} + W_{o2} + W_{p2} + W_{p2}^*$

$W_{p2}^* = c \times S_{p2}^* \times M_{p2}^*$

Where c = 0.88 (from pryrite analysis, but should be 1.000 for pure FeS_2)

$S_{p2}^* = 2 \times 32.06 / (55.8475 + 2 \times 32.06) = 0.53448$

$W_{p2}^* = 0.88 \times 0.53448 \times M_{p2}^*$

$= 0.47034 \times M_{p2}^*$

$W_{o1} + W_{o2} + W_{p2} = 100 \times (S_{o1} + S_{o2} + S_{p2})$: constant for a coal

$W_T = 100 \times (S_{o1} + S_{o2} + S_{p2}) + 0.47034 \times M_{p2}^*$

$= 100 \times S_{o1} + (100 \times (S_{o2} + S_{p2}) + 0.47034 \times M_{p2}^*)$

$= 100 \times S_{o1} + (100 \times (A_{o2} + S_{p2}) + W_{p2}^*)$

$= W_1 + W_2$

Where $W1 = 100 \times S_{o1}$ (constant)

$W_2 = 100 \times (S_{o1} + S_{p2}) + 0.47034 \times M_{p2}^{*}$

$= 100 \times (S_{o2} + S_{p2}) + W_{p2}^{*}$

$W_i = a \times A_i$

One can obtain the area of peak 1 (A_1) and peak 2 (A_2) and total sulphur content (S_T) from infrared SO_X spectrochronograms of coal. Either a single sample of coal or a multiple of mixed samples (CASES I & II) may be analysed to provide the same informatin. Sulphur contents represented by peak 1 (S_1) and peak 2 (S_2) can be obtained from the ratio of peak area. The following definition is obvious.

$S_T - S_{SO4} = S_{o1} + S_{o2} + S_{p2}$

$= S_1 + S_2$

$= S_{oT} + S_{pT}$

Where $S_1 = S_{o1}$

$S_2 = S_{o2} + S_{p2}$

$S_{oT} = S_{o1} + S_{o2}$

$S_{pT} = S_{p2}$

Experimental data gives the value for S_1 and S but not for the detailed value for S_{o2} and S_{p2}. These can be obtained if a ratio between the contents of different sulphur forms remains constant, as discussed the linear regression analysis of different sulphur forms in various coals by Yurovskii, A.Z. (2). Modification of this analysis yields:

$$S_T = 0.51560 + 1.35685 \times S_{pT}$$

The following three cases were considered for which the ratio between the contents of different sulphur forms remain constant.

Case A. : $k = S_{o1} / S_{p2}$

$$S_T - S_{SO4} = S_{o2} + (1 + k) \times S_{p2}$$

Case B. : $m = S_{o2} / S_{p2}$

$$S_T - S_{SO4} = S_{o1} + (1 + m) \times S_{p2}$$

Case C. : $n = S_{o2} / S_{o1}$

$$S_T - S_{SO4} = (1 + n) \times S_{o1} + S_{p2}$$

A. If constant k (= S_{o1} / S_{p2}) is known :

$$S_T - S_{SO4} = S_{o1} + S_{p2}$$
$$= k \times S_{p2} + S_{o1} + S_{p2}$$
$$= S_{o2} + (1 + k) \times S_{p2}$$

Problem Solving Procedure;

1. S_{o1} and S_2 from analysis
2. $S_{p2} = S_{o1} / k$
3. $S_{o2} = S_2 - S_{p2}$
   $= S_2 - S_{o1} / k$
4. $S_{oT} = S_{o1} + S_{o2}$
   $= S_2 + (1 - 1/k) \times S_{o1}$
5. $S_T - S_{SO4} = S_{oT} + S_{p2}$
   $= S_{o1} + S_2$

Q.E.D.

B. If constant m (= S_{o2} / S_{p2}) is known :

$$S_T - S_{SO4} = S_{o1} + S_{o2} + S_{p2}$$
$$= S_{o1} + m \times S_{p2} + S_{p2}$$
$$= S_{o1} + (1 + m) \times S_{p2}$$

Problem Solving Procedure;

1. S_{o1} and S_2 from analysis
2. $S_{p2} = S_2 / (1 + m) = S_{pT}$
3. $S_{o2} = m \times S_{p2}$
4. $S_{oT} = S_{o1} + S_{o2}$
   $= S_{o1} + (m / (1 + m)) \times S_2$
5. $S_T - S_{So4} = S_{oT} + S_{pT}$
   $= S_{o1} + S_2$

Q.E.D.

C. If constant n (= S_{o2} / S_{o1}) is known :

$$S_T - S_{SO4} = S_{o1} + S_{o2} + S_{p2}$$
$$= S_{o1} + n \times S_{o2} + S_{p2}$$
$$= (1 + n) \times S_{o1} + S_{p2}$$

Problem Solving Procedure;

1. S_{o1} and S_2 from analysis
2. $S_{o2} = n \times S_{o1}$
3. $S_{p2} = S_2 - S_{o2}$
   $= S_2 - n \times S_{o1}$
4. $S_{oT} = S_{o1} + S_{o2}$
   $= (1 + n) \times S_{o1}$
5. $S_T - S_{SO4} = S_{oT} + S_{p2}$
   $= S_{o1} + S_2$

Q.E.D.

CURRENT EXAMPLE OF CASE I-A

$$W_1 = 100 \times S_{o2} + S_{i1} \times W_{p2}^* / 0.47034$$

$$W_2 = 100 \times (S_{o2} + S_{p2}) + (0.47034 - (S_{o2} + S_{p2})) \times W_{p2}^* / 0.47034$$

$$= 100 \times S_2 + (0.47034 - S_2) \times W_{p2}^* / 0.47034$$

Data from experiments : $A_2 = 498.04 + 534.66 \times W_{p2}^*$

(Figure 1)

Assuming $W_2 = a \times A_2$;

$100 \times S_2 = 498.04 \times a$

$(0.47034 - S_2) / 0.47034 = 534.66 \times a$

Therefore $a = 1.83402 \times 10^{-3}$

$S_2 = 9.13416 \times 10^{-3}$

Experimental data at $W_{p2}^* = 0$;

i	** A_i	A_i/A_T	S_i(%)
1	71.34	0.11075	0.12072
2	572.82	0.88925	0.96928
.....	.....	.....	.....
T	644.16	1.00000	1.09000

** Experimental peak area in arbitrary units per mg of coal sample

Experimental results are given in Figures 1, 2 and 3. According to Figure 1, the total sulphur content in the coal sample is 0.93151%. The standard assay value is 1.11%. Figure 2 indicates that the present procedure results in a more reliable S_{o2} reproduciblity.

Case I-A. : $k = S_{o1} / S_{p2}$ (constant)

$$S_T - S_{SO4} = S_{o2} + (1 + k) \times S_{p2}$$

$S_1 = S_{o1} = 0.12072$ (%)

$S_2 = S_{o2} + S_{p2} = 0.96928$ (%)

$S_T = S_1 + S_2 = 1.09000$ (%)

If $k = S_{o1} / S_{p2}$ (= 0.31768) is known,

$S_{pT} = S_{p2} = S_{o1} / k = 0.12072 / 0.31768 = 0.38000$ (%)

$S_{o2} = S_2 + S_{p2} = 0.96928 - 0.38000 = 0.58928$ (%)

$S_{oT} = S_T - S_{p2} = 1.09000 - 0.38000 = 0.71000$ (%)

$= S_{o1} + S_{o2} = 0.12072 + 0.58928 = 0.71000$ (%)

$$S_T - S_{SO4} = S_{o2} + (1 + k) \times S_{p2}$$
$$= 0.58928 + 1.31768 \times S_{p2}$$

This is very similar to the modified Yurovskii's Regression Equation, i.e.,

$S_T = 0.51560 + 1.35685 \times S_{pT}$

CONCLUSION

The present discussion has demonstrated that organic and pyritic sulphur contents can be quantitatively determined from experimental peak area (A_1 & A_2), total sulphur content (S_T) and the constant rario of k between organic sulphur 1 (S_{o1}) and pyritic sulphur (S_{p2}).

REFERENCE

1. Dancziger, M., "Progress Report - Development of CANMENT SULPHUR FORM ANALYSER", Barringer Research Ltd., September 1987.

2. Yurovskii, A.Z., 1974, Sulphur in Coals, TT 70-57216, Academy of Sciences of the USSR Institute of Mineral Fuels, Translated from Russian for the U.S.B.M. and NSF, Washington, by the Indian National Documentation Centre, New Dehli, 453 p.

Figure 1 : A_2 vs Pyritic Sulphur Added

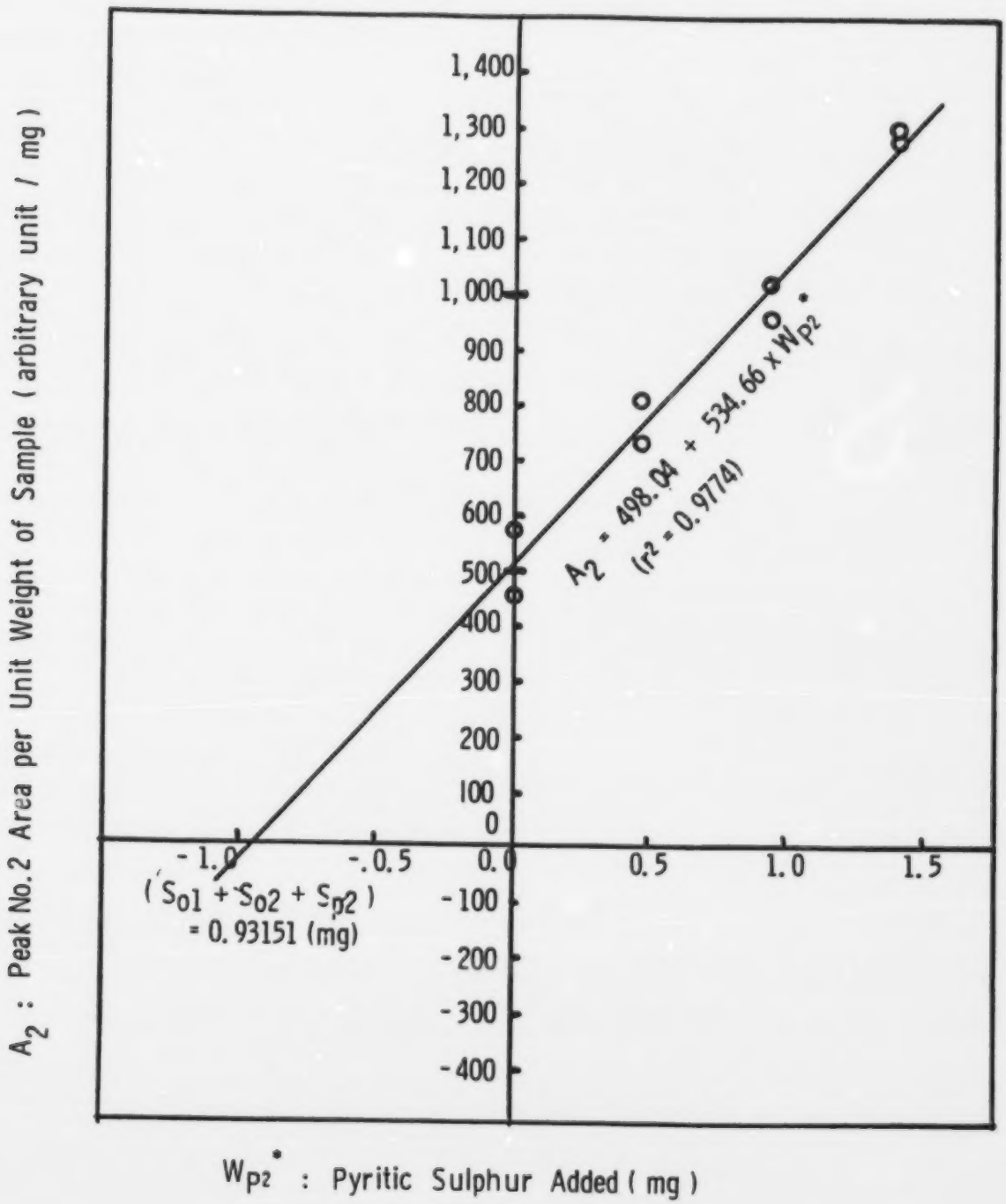

Figure 2 : A_1 vs Total Sulphur Content

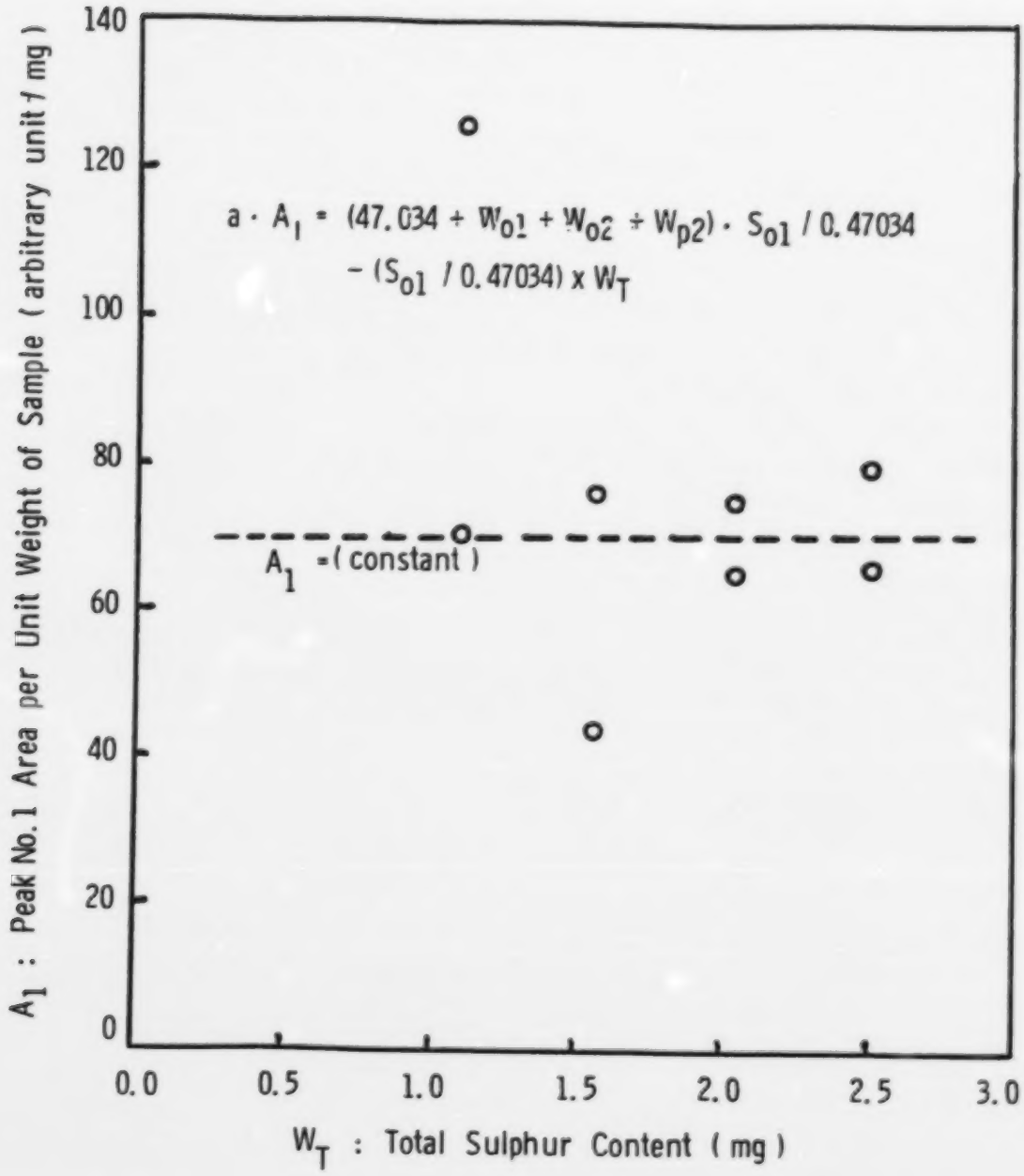

Figure 3 : A_T vs Total Sulphur Content